

ORGANIC AND INORGANIC GEOCHEMISTRY OF COAL

Fangui Zeng

Shanxi Key Laboratory of Coal Science and Technology, Taiyuan University of Technology, China

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Contents

1. Introduction
2. Organic Geochemistry of Coal
 - 2.1 Origin of Coal and Coal Macerals
 - 2.1.1 Origin of Coal
 - 2.1.2 Coal Macerals
 - 2.2 Peatification and Coalification
 - 2.2.1 Peatification
 - 2.2.2 Coalification
 - 2.3 Soluble Substances in Coals
 - 2.3.1 Characteristics of Soluble Substances in Coals
 - 2.3.2 Biomarkers in Soluble Materials from Coals
 - 2.3.3 Hydrocarbons Derived from Coal
 - 2.4 Coal Structure
 - 2.4.1 Concept of Coal Structure
 - 2.4.2 Chemical Structure of Coals
 - 2.4.3 Physical Structure of Coal
 - 2.5 Prospects in Organic Geochemistry of Coal
 - 2.5.1 Coalification and Hydrocarbons Derived from Coal
 - 2.5.2 Computer Simulation of Coal Structure
3. Inorganic Geochemistry of Coal
 - 3.1 Origin of Inorganic Substances in Coal
 - 3.1.1 Minerals of Plant Origin
 - 3.1.2 Minerals of Detrital Origin
 - 3.1.3 Minerals of Chemical Origin
 - 3.1.4 Formation Stages of Minerals in Coal
 - 3.2 Trace Elements in Coal
 - 3.2.1 Classification of Trace Elements
 - 3.2.2 The Occurring Form of Trace Elements in Coal
 - 3.2.3 The Correlation of Contents of The Trace Elements with Macerals, Minerals and Coal Rank
 - 3.2.4 Enrichment of Trace Elements in Coal

3.3 Environmental and Geological Implication of Trace Elements in Coal

3.3.1 Influence of Trace Elements in Coal on the Environment

3.3.2 Geological Implication of Trace Elements in Coal

3.4 Prospects in Inorganic Geochemistry of Coal

Glossary

Bibliography

Biographical Sketch

Summary

Coal is an aggregate of heterogeneous materials composed of organic and inorganic substances. Therefore, the geochemistry of coal deals with the origin, evolution, and environmental effects of organic and inorganic substances in coal and the formation, evolution, and appraisal of the mineral deposits relating to coal. In this article, some fundamental knowledge on coal geochemistry, and its recent main developments are introduced. Macerals, the organic part of coal originated from plant remains, are the products of peatification and coalification. In the peatification process, the plant remains have undergone biochemical change. After the burial of peat, the coalification process takes place, which results in the biogeochemical and geochemical alteration of peat and early-formed coal and the formation of macerals. In the coalification process, natural gas (also called gas derived from coal) and petroleum (oil derived from coal) reservoirs can be formed under the appropriate geological conditions. Because the four “jumps” which exist in coalification result in the salient alteration of physical and chemical properties of coal, knowledge of the evolution of coal structure is necessary and important for understanding the nature of these jumps. In recent years, a more refined information about coal structure has been obtained and some concepts of coal structure have been, are being, and will be, changed. Through the investigation of coalification and hydrocarbon derived from coal, the coal/fluid interaction can be understood and a series of new research approaches for coal, such as computer simulation, thus be developed.

Inorganic substances in coal include minerals, mainly Si, Al, and Fe, etc., and trace elements, excluding C, H, O, N, S, and Si, Al and Fe, etc. According to their origin, the inorganic substances can be classified into three types: plant, detrital, and chemical origin in two distinct stages—the syngenetic and epigenetic stages. Based upon the effect of trace elements on environment and health, they can be classified into six types.

- those which have a severe effect on the environment
- those which have a secondary influence on the environment
- those whose effect is slight
- radioactive types
- those which rarely accumulate in coal and coal ash
- those which do not pollute the environment to any extent

Recently, increasing attention has been paid to the effect of inorganic substances in coal on environment and health.

1. Introduction

Since the microscope was used to investigate coals in the early twentieth century, and macerals have been found and given a terminology, their origin and evolution, and their correlation with other mineral deposit, such as the petroleum and natural gas in crust, have been the main subjects of organic geochemistry. A combination of coal petrology and organic geochemistry has become an important method for the appraisal of petroleum and natural gas. Recently, special interests have been the formation, evolution, and appraisal of the oil derived from coal and the development of new research approaches in the organic geochemistry of coal, such as the computer simulation method.

The inorganic geochemistry of coal deals with the origin and evolution of inorganic materials (i.e. minerals and trace elements) in coal. Recently, more attention has been paid to the correlation of inorganic materials with organic materials (i.e. macerals) and the effect of inorganic materials in coal on the environment and the human body.

2. Organic Geochemistry of Coal

2.1 Origin of Coal and Coal Macerals

2.1.1 Origin of Coal

Coal is an aggregate of heterogeneous materials composed of organic and inorganic substances. All coal deposits were formed in the peat swamps. Different types of plant flourished in the peat swamps, which primarily reflect the conditions of climate, water level, and water chemistry of the swamps. The organic materials are derived mainly from plant remains, which have undergone various degrees of decomposition in the peat swamps, and physical and chemical alteration after burial. The formation of the peat swamps depends on following factors: the evolutionary development of plants, climate, and the geographical and structural position of the region.

Plant evolution played an important part in the makeup of the plant source material in a swamp, ultimately affecting the petrologic composition of the coal. Coals forming in a peat swamp are essentially *in situ* in origin. On the other hand, some peat and even coals may be reworked and re-deposited in a fluvial system and are called *allochthonous* in origin. Coal deposits derived from extensive accumulation of driftwood also belong to this category.

If the accumulating peats are subsequently buried and preserved, any region where conditions are favorable for the accumulation of peat, is a potential region for coal formation. The back swamps of floodplain, lake margins, lagoons and coastal plains where tidal fluctuation is low, and glaciated regions with poor drainage are all good environments for peat accumulation. The conditions for producing thick layers of coal are that the region must be constantly subsiding, or the groundwater level must be rising slowly but steadily, and the accumulation of plant debris must keep pace with the rising water level.

2.1.2 Coal Macerals

Optically homogeneous discrete organic material in coal is named maceral (derived from the Latin *macerare*, to macerate, to separate). All macerals are classified into three groups: vitrinite, exinite (or liptinite), and inertinite. Macerals are derived from and named after the particular plant tissues commonly preserved in peat swamps. Vitrinite is derived from variously decomposed woody tissues, and exinite is derived from spore and pollen coats, cuticles, resins, and other fatty secretions. On the other hand, inertinites are derived from the partial carbonization by fire of various plant tissues in the peat swamps stage, and others are perhaps derived from intensive chemical degradation induced by microorganisms. Each group includes a series of macerals, which can be regarded as belonging together, either because of similar origin (such as exinite), or because of the mode of conservation (vitrinite and inertinite). Table 1 shows the classification of the macerals of hard coals. The macerals of lignite (or brown coals) are different from those of the hard coals. Table 2 shows the classification of the macerals of lignite. From Tables 1 and 2, it can be found that huminite in lignite is transformed into the vitrinite of hard coals during coalification.

Maceral Group	Maceral	Submaceral	Maceral Variety
Vitrinite	Telinite	Telinite 1 Telinite 2	Cordaitotelinite Lepidophytotelinite Conifero- ginkgophytotelinite Sigilariotelinite Fungotelinite
	Collinite	Telocollinite Desmocollinite Gelocollinite Corpocollinite	
	Vitrodetrinite		
Semivitrinite	Semitelinite		
	Semicollinite	Telosemicollinite Desmosemicollinite Corposemicollinite	
	Semivitrodetrinite		
Inertinite	Fusinite	Pyrofusinite Degradofusinite	Lepidophytofusinite Psaroniofusinite Conifero- ginkgophytofusinite
	Semifusinite		
	Macrinite	Macrinite 1 Macrinite 2	
	Micrinite		
	Sclerotinite	Sclerotinite 1 Sclerotinite 2	
	Inertodetrinite		
Lipitinite (Exinite)	Sporinite	Macrosporinite Microsporinite	

	Cutinite Suberinite Barkinite Resinite		
	Alginite	Telalginite Lamalginite	Pila-alginite Reinschia-alginite
	Bituminite Exsudatinitite Fluorinitite Lipitodetrinitite		

Table 1. Classification of macerals of hard coals

Maceral Group	Maceral Subgroup	Maceral	Maceral Type	Maceral Variety
Huminite	Humotelinitite	Textinitite		Pinotextinitite Betulotextinitite Taxodiotextinitite Fungotextinitite
		Ulminite	Texto-ulminite Eu-ulminite	
	Humodetrinitite	Attrinitite		
		Densinitite		
	Humocollinitite	Gelinitite	Porigelinitite Levigelinitite	
		Corpohuminitite	Phlobaphinitite Pseudo-phlobaphinitite	
Lipitinitite		Sporopolleninitite	Macrosporinitite Microsporinitite Polleninitite	Pinopolleninitite
		Cutinite		
		Resinitite		
		Suberinitite		
		Chlorophyllinitite		
		Bituminite		
		Exsudatinitite		
		Fluorinitite		
		Alginite		
		Lipitodetrinitite		
Inertinitite		Fusinitite		
		Semifusinitite		
		Macrinitite	Primary Macrinitite Oxymacrinitite	
		Sclerotinitite		
		Inertodetrinitite		

Table 2. The Classification of macerals of lignite

Vitrinite is the most frequent and important maceral group occurring in bituminous coals. Cellular structures derived from vegetable material are sometimes visible in vitrinite under microscope. The cell walls are called telinite. In many cases it is difficult to distinguish between telinite and collinite so that they both tend to be recorded as vitrinite in maceral analyses. Pure telinite is rare. Telinite and vitrinite generally originate from trunks, branches, stems, leaves, and roots. Among the three maceral groups, vitrinite has a medium level of reflectance, carbon, and hydrogen content.

The exinite group consists of sporinite, cutinite, suberinite, resinite, alginite, and liptodetrinite. In low rank coals, the exinites are distinguished from the vitrinite by a higher hydrogen content. On Carbonization they yield much tar and gas. In high volatile bituminous coals (more than 30% V.M. in the vitrinite) the exinites more or less maintain their composition. But with the transition from high to medium volatile bituminous coals, at a V.M. yield of 28%, they undergo a relatively rapid change that is called as the “coalification jump.”

The inertinite group comprises the macerals fusinite, semifusinite, macrinite, micrinite, sclerotinite, and inertodetrinite. The characteristic optical property of inertinite macerals is their high reflectance. Among the three maceral groups, the fusibility of the inertinite macerals in coking coals is weak or nil. Therefore, the word “inert” is to describe more or less non-reactivity of inertinites. But micrinite is not inert. In fact, it differs in its origin from the rest of the inertinites.

2.2 Peatification and Coalification

2.2.1 Peatification

Peatification, also called “biochemical coalification,” includes microbial and chemical alteration. In the peatigenic layer (from peat surface to a depth of approximately 0.5m), the most severe alteration takes place. In this layer, aerobic bacteria, actinomyces and fungi are active. With the increment of depth, these organisms are replaced by anaerobic bacteria, but as the easily assimilated substances disappear, microbial life is reduced and finally extinguished, usually at depths of less than 10m, below which only chemical changes occur, mainly condensation, polymerization, and reducing reactions.

Humification is the most important process during peatification. It forms the humic substances. The degree of humification depends on the oxygen supply, the peat temperature, and the pH values of water in the peat swamps.

Since the relatively oxygen-rich materials in the peatigenic layer, particularly cellulose and hemicellulose, are decomposed microbiologically, which results in an enrichment of relatively carbon-rich lignin and the newly-formed humic acids, in a peat profile the carbon content increases rapidly with depth. A rise in carbon from 45–50% to 55–60% is quite possible in the peatigenic layer, but at greater depths the carbon content hardly changes. With increasing depth, the moisture content falls rapidly. The free cellulose can also be found in peats and is an indicator of degree of peat diagenesis. Therefore, in order to distinguish between peats and soft brown coals, moisture and carbon contents, the presence of free cellulose are used as parameters.

2.2.2 Coalification

The development from peat through the stages of the different brown coals (lignite), sub-bituminous coals to anthracites and meta-anthracites is called coalification.

If the degree of chemical and physical alteration is taken as its basis, then coalification can only be regarded as a diagenetic process up to the stage of mature soft brown coals. From the beginning of the hard brown coal (sub-bituminous) stage, the alteration of organic material is so severe that it must be regarded as metamorphism, although the essential conditions (temperature, time and pressure), which are necessary for the formation of bituminous coals, produce only weak, diagenetic changes in the associated sediments.

The coalification behavior of the individual macerals is different (Fig.1). Therefore, the comparative rank studies are not carried out on whole coals, but only on the huminites-vitrinites or the concentrates of these macerals.

The fall in moisture content is the primary characteristic with increasing rank at the brown-coal stage. The decrease in porosity and the decomposition of the functional groups bearing oxygen, result in a fall in the moisture content. At this stage, hydrophylic, carboxyl, methoxyl, and carbonyl functional groups are markedly spilt off, and the carbon content gradually rises.

During the hard brown-coal (lignite to sub-bituminous) stage, the remnants of lignin and cellulose are transformed into humic materials and the humic acids condense to larger molecules, losing their acid character to form alkali-insoluble humines.

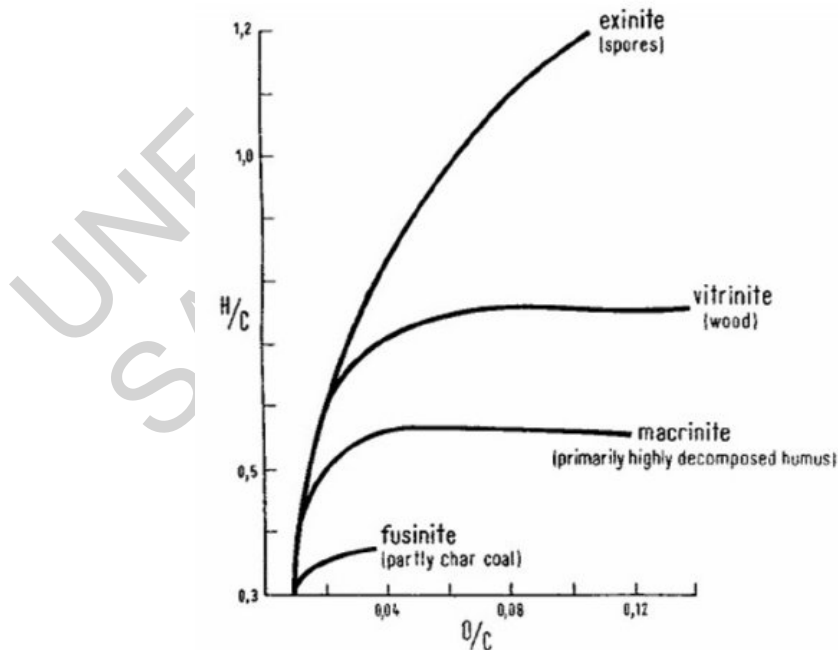


Figure 1. Coalification tracks of different macerals based on H/C: O/C atomic ratios (after van Krevelen)

Carbon dioxide, water, and some methane are yielded at this stage. Recent investigation shows that if coals are rich in resinite, some liquid hydrocarbons are produced in these stages and under appropriate geological conditions they are able to form the so-called “immature oil” reservoir. The petrographic changes taking place at the boundary of the dull/bright brown-coal stage are very striking. The geochemical gelification (also called vitrinitization) of humic substances is typical of this stage. It results in coals becoming black and lustrous.

The progress of coalification in the high-volatile bituminous coals (>30% V.M. (daf)) is similar to that in the brown coals. In the later bituminous-coal stages (<30%–10% V.M.), volatile matter, which consists mainly of the non-aromatic fraction of coal, falls rapidly due to the removal of aliphatic and alicyclic groups and the increasing aromatization of the humic complexes.

The anthracite stage is characterized by a rapid fall of hydrogen content and of atomic H/C ratio, and by a particularly strong increase of reflectivity and also of optical anisotropy.

It must be emphasized that in the coking-coal range (ca. 87–89% carbon), many properties pass through a maximum or a minimum value. Because in the earlier bituminous-coal stages, oxygen-rich products (carbon dioxide and water) are mainly released, while substantial losses of methane begin much later (<29% volatile matter), at this rank most of the oxygen is lost, whereas the hydrogen content is still high.

Four coalification jumps occur during the whole coalification process. The first coalification jump takes place at the sub-bituminous coal (80% Cdaf, 43% V.M., 0.6% R^o_m) stage, and so-called “bituminization” is the main characteristic. The second begins at coking-coal range (87% Cdaf, 29% V.M., 1.3% R^o_m). As previously mentioned, in this range many properties have passed through a maximum or minimum, and so the second coalification jump is also called the coalification break. The third stage takes place at the boundary (91% Cdaf, 8% V.M., 2.5% R^o_m) of bituminous coals and anthracite, and the fourth begins at the boundary (93.5% Cdaf, 4% V.M., 3.7% R^o_m) of anthracite and meta-anthracite.

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Biographical Sketch

Fangui Zeng, is the postdoctoral researcher of Shanxi Key Lab. of Coal Science and Technology and one of the academic staff of the College of Mining Engineering, Taiyuan University of Technology, China. He gained his Masters degree in Xi'an Mining Institute, China, on June, 1991. His Ph.D. was awarded by China University of Mining and Technology on June, 1997. Recently, his research interest is the computer simulation of coal structure evolution during coalification and coal/fluid interaction.